

A CASSCF-CASPT2 Study of the Excited-State Intramolecular Proton Transfer Reaction in 1-Amino-3-Propenal Using Different Active Spaces

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ABSTRACT: In this work we analyze how the choice of the active space in the CASSCF (the complete-active-space multiconfiguration self-consistent-field method) and CASPT2 (the second-order perturbation theory based on the CASSCF reference wave function) calculations affects the computed potential energy curves (PECs) for the intramolecular proton transfer reaction in the ground state and the two lowest lying singlet excited states of 1-amino-3-propenal. As anticipated, the results revealed that, qualitatively, the proton transfer in the different states can be correctly described even by minimal active spaces, which include the orbitals involved in the electronic excitation of the considered state and the antibonding sigma orbital corresponding to the bond formed by the molecule with the migrating hydrogen atom. However, quantitatively, the relative energies of the two tautomers and the energy barriers computed at the CASSCF level change when the active space is increased, indicating importance of the dynamic electron correlation. Introducing the dynamic correlation effects via CASPT2 makes the calculated energy parameters more uniform among the different active spaces. The analysis suggested certain optimal active spaces for studying proton transfer reactions in systems similar to 1-amino-3-propenal. The PEC calculations for excited states showed that the results are sensitive to the molecular geometries used in the calculations,

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particularly near the transition point. © 1999 John Wiley & Sons, Inc. J Comput Chem 20: 1422–1431 (1999)

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Introduction

One of the techniques that has been extensively used to study electronic excited states in molecules is the complete-active-space multi-configuration self-consistent-field (CASSCF) method.¹ This methodology has been applied in the recent years to study electronic spectra of organic and inorganic molecules.^{2–20} In general, the results have proven that the CASSCF method yields a balanced description of the electronic states and provides reliable predictions of physical properties and transition dipoles. However, in most cases it has not been possible to compute with high accuracy the transition energies because the CASSCF wave function includes only a fraction of the electron correlation. To account for the remaining electron correlation effects one needs to go beyond the CASSCF level of approximation. One of the most computationally reliable methods available at present is probably the multiconfiguration second-order perturbation theory (CASPT2) method.^{21–23} In this method the CASSCF wave function is used as a reference function. The behavior of the CASPT2 method has been discussed in detail in some earlier applications.^{2, 3, 5–8, 10–14, 16–20} The present calculations on the proton transfer pathways in the ground and the two lowest-lying singlet excited states of 1-amino-3-propenal provide an additional contribution to this analysis.

The crucial element in performing CASSCF calculations is to correctly choose the active orbital space and the number of active electrons. This task is far from being straightforward, particularly in situations where chemical bonds are elongated and simultaneously the molecule is excited to a higher electronic state. The choice of the active orbitals requires an insight into the electronic structure of the molecule at all stages of the process under consideration. In some cases this choice is obvious, for example, in the case of rupturing a chemical bond in the ground electronic state, the bonding and the antibonding orbitals for the ruptured bond

should be included in the active space. However, in situations where the molecule undergoes a more complex transformation, the choice is often not as clear, and several trials are necessary before the right active space is found.

There are some approximate criteria that one can use in selecting the active space. For example, the occupation numbers of the natural orbitals derived from the unrestricted Hartree–Fock (UHF) calculation provide indication of the importance of a particular orbital in the wave function. Typically, valence orbitals with occupation numbers above 0.02 are included in the active space.^{24, 25} Also, a single-point CI calculation followed by analysis of the occupation numbers of the natural orbitals derived from the CI density matrix can be used in selecting the active space.²⁶ In general, when a more extended range of the potential energy surface (PES) is considered, the natural orbitals analysis should be performed at different geometries to select a uniform active space that provides a balanced treatment along the whole PES.

In calculating electronic spectra, the active orbital space^{2, 3, 5–18} is usually determined based on the type of excitation considered. The convergence of the computed transition moment between the calculated states with the size of the active orbital set has been used as a criterion for selecting the active orbitals.²⁷ Another possibility is to use the single excitation configuration interaction (SCI) method and select the orbitals that are present in the most important configurations in the considered states. This approach was used in the calculations of the excited-state intramolecular proton transfer (ESIPT) reaction in 1,5-Diaza-1,3-pentadiene.²⁸ However, because SCI cannot properly describe the bond dissociation due to its lacking higher excited configurations—even a description of a single-bond dissociation requires doubly excited configurations in the wave function—the use of this criterion may lead to an inadequate active space. Moreover, even in cases when one is able to select an adequate active space, it may happen that it is computationally intractable due to its size and a smaller space needs to be considered.¹³

In conclusion, the selection of the active space is a problem that needs to be considered individually on a case-by-case basis. One can use one of the criteria mentioned above or a combination of the criteria. In the present study, we analyze the selection of the active orbital space for a system that simultaneously undergoes an electron excitation and a bond rearrangement. This type of problem exemplifies one of the most difficult cases for CASSCF and CASPT2 calculations. More specifically, we are interested in the ESPT in 1-amino-3-propenal (see Fig. 1). The ESPT processes have been studied before for different molecules^{28–33} using the CASSCF/CASPT2 methods. Particularly, the proton transfer in 1-amino-3-propenal was already investigated at the CASSCF level.³¹ However, in that study no systematic analysis of the active space selection was presented, and no CASPT2 results were included.

1-Amino-3-propenal is a good model system to study proton transfer reactions occurring along an intramolecular hydrogen bond. Similar reactions in related systems have been studied experimentally.^{34–37} Although a system as small as 1-amino-3-propenal is usually difficult for experimental investigations and larger molecules with more definite backbones are preferred, in the theoretical calculations larger molecules can only be studied at lower levels of approximation with methods like SCI.^{38–40} More sophisticated methods, like CASSCF and CASPT2, are needed if a more quantitative information is required.⁴¹ However, for larger systems CASSCF and CASPT2 calculations are usually prohibitively expensive to perform, particularly with large active spaces. If, however, the number of active orbitals can be reduced without significant loss of accuracy, one can also study these types of systems at the CASSCF or even CASPT2 levels. In the present calculations on 1-amino-3-propenal we analyze whether and to what level such a reduction is possible.

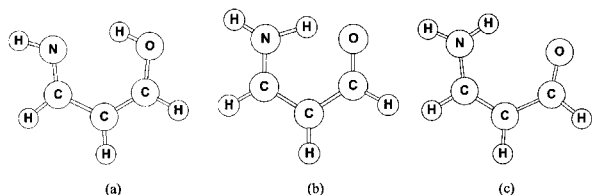


FIGURE 1. (a) enol, (b) transition state, and (c) keto forms optimized in the ground electronic state at the CASSCF level.

Computational Details

Calculations of the PEC for the intramolecular proton transfer in the ground state and the two lowest-lying singlet excited states of 1-amino-3-propenal, which result from the $n\pi^*$ and $\pi\pi^*$ excitations, were first done with the CASSCF method.¹ In the present calculations the molecular geometries were first optimized using the Hartree–Fock (HF) method for the ground state and the configuration interaction method with singly excited determinants (CIS) for the excited states. The UHF and CASSCF geometry optimizations were also performed. In the optimizations the bond length between the hydrogen and nitrogen atoms was assumed to be the reaction coordinate, and was incrementally changed to move the hydrogen atom between the two minima corresponding to the two tautomers while all the other coordinates were fully optimized. The symmetry of 1-amino-3-propenal was restricted to C_s . Because polarization functions are important in describing valence excited states,^{8,42} we used the double-zeta-valence Gaussian basis set of Dunning and Hay with polarization functions.⁴³ In some calculations we also augmented the Dunning and Hay basis set with additional diffuse functions.⁴⁴

The major virtue of CASSCF is that it is capable of describing the nondynamical electron correlation in a size-consistent and balanced way in situations when the electronic structure strongly changes, as it happens near transition states and in electronic excitation processes. The CASSCF wave function is an expansion in terms of spin-adapted configuration state functions (CSFs) which are formed by distributing the active electrons among the active orbitals in all possible ways consistent with the given total spin and space symmetry. The CSFs are expressed as linear combinations of Slater determinants (SDs), which are constructed from symmetry adapted orbitals. The orbital space is divided into three subspaces: the inactive, active, and secondary orbitals. The inactive orbitals are doubly occupied in all CSFs. Both inactive and active orbitals are variationally optimized in the CASSCF calculation by mixing them with the secondary orbitals that are not occupied.

We used the “(kl;m)” notation to denote the CASSCF active space used in the calculations. The first two indices in (kl;m) indicate the number of active orbitals in the two irreducible representations of the C_s point group, a' and a'' , and the last

number indicates the number of electrons. We considered the following active spaces in the calculations: (2, 2; 4), (2, 4; 6), (2, 5; 8), (3, 4; 8), (4, 4; 10), (6, 4; 10), (6, 6; 6), (6, 6; 8), (6, 6; 10), (6, 6; 12), (4, 8; 10), and (3, 6; 10). For each of the state and for each of the active space the electronic energy was calculated in 11–12 points on PECs corresponding to the ground and excited states. To assure a smooth behavior of PEC the orbital optimization for each point was almost always initiated with the orbitals obtained from the previous point. The CASSCF calculations for each state were performed separately.⁹

The CASSCF wave function mainly describes the nondynamic electron correlation effects. To account for the dynamic electron correlation effects we used the CASPT2 method.^{21–23} A CASPT2 calculation was done at each point of PEC and for each active space considered. The CASPT2 method computes the first-order wave function and the second-order energy with the CASSCF wave function as the reference function. The zeroth-order Hamiltonian is defined using Fock-type one-electron operators, and is constructed in such a way that for the closed-shell single determinant case the CASPT2 method becomes equivalent to the conventional MP2 (Møller–Plesset second-order) perturbation theory. Two different formulations of the zeroth-order Hamiltonian are possible: one that includes only the diagonal part of the Fock matrix (PT2D), and one that includes also the nondiagonal elements (PT2F). The latter one was applied in the present study. All the reported calculations were performed using the MOLCAS-3 and -4 quantum chemistry software packages.^{45,46}

Results and Discussion

Because we consider the $n\pi^*$ and $\pi\pi^*$ electronic transitions, one of the smallest active spaces that can simultaneously describe these excitations is (2, 2; 4), where the four electrons occupying the highest π and n orbitals are excited to the π and σ antibonding orbitals. Next, we systematically increased the number of active orbitals and correlated electrons in the CASSCF wave function to see what effect this has on the results. First, we extended the active space to (2, 4; 6) by including the second highest π double occupied orbital and the second lowest π virtual orbital. We continued adding more orbitals into the active space: the third highest π occupied orbital to form the (2, 5; 8)

space, the next highest σ occupied orbital to form the (3, 4; 8) space, the third lowest π virtual orbital to form the (3, 6; 10) space, and the following highest σ occupied orbital to form the (4, 4; 10) space. Next, we extended the (4, 4; 10) space by adding two σ virtual orbitals to get the (6, 4; 10) space. The largest active space considered was (6, 6; 12), where the highest π and σ valence electrons were distributed among 12 active orbitals, six of the A' symmetry and the other six of the A'' symmetry. We also analyzed what effect the number of active electrons may have on the results by considering the following series of active spaces: (6, 6; 12), (6, 6; 10), (6, 6; 8), (6, 6; 6), and (4, 8; 10).

The CASSCF energy profiles for the proton transfer reaction along the NH-stretching reaction coordinate calculated for the ground state, and the $n\pi^*$, and $\pi\pi^*$ excited states using the different active spaces, are plotted in Figures 2a, b, and c, respectively. As expected, with the increase of the active space the energies get lower. The smallest (2, 2; 4) active space gives the highest energy values for all the considered states. When two a'' orbitals are added to the active space the energy along the reaction coordinate decreases considerably for all the states. Whereas the (2, 4; 6) and (2, 5; 8) active spaces give similar energy values in the $n\pi^*$ excited state, the energy decreases significantly in this state when an additional a' occupied orbital is added to the (2, 4; 6) space. This is an expected result because this excited state results from an electronic transition from an n orbital, which has the a' symmetry, to a π^* orbital. By contrast, including an additional a'' occupied orbital in the (2, 4; 6) active space affects the PEC of the $\pi\pi^*$ state more than including an a' orbital. As expected, the largest active space, (6, 6; 12), yields the lowest energy values.

One notices that all active spaces considered, correctly describe the three most important characteristics of the proton transfer reaction in 1-amino-3-propenal, showed already by Domcke and Sobolewsky,³¹ i.e., the higher stability for the keto form than for the enol form in all the three studied states, a large energy barrier in the $n\pi^*$ excited state than in the ground state and no barrier in the $\pi\pi^*$ excited state. It should be mentioned that in the calculations of Domcke and Sobolewski the molecular geometries were optimized in the ground state at the CASSCF level with the (3, 4; 8) active space, and were not reoptimized for the excited states.

Similar results obtained for all the active spaces indicate that a qualitative description of the proton

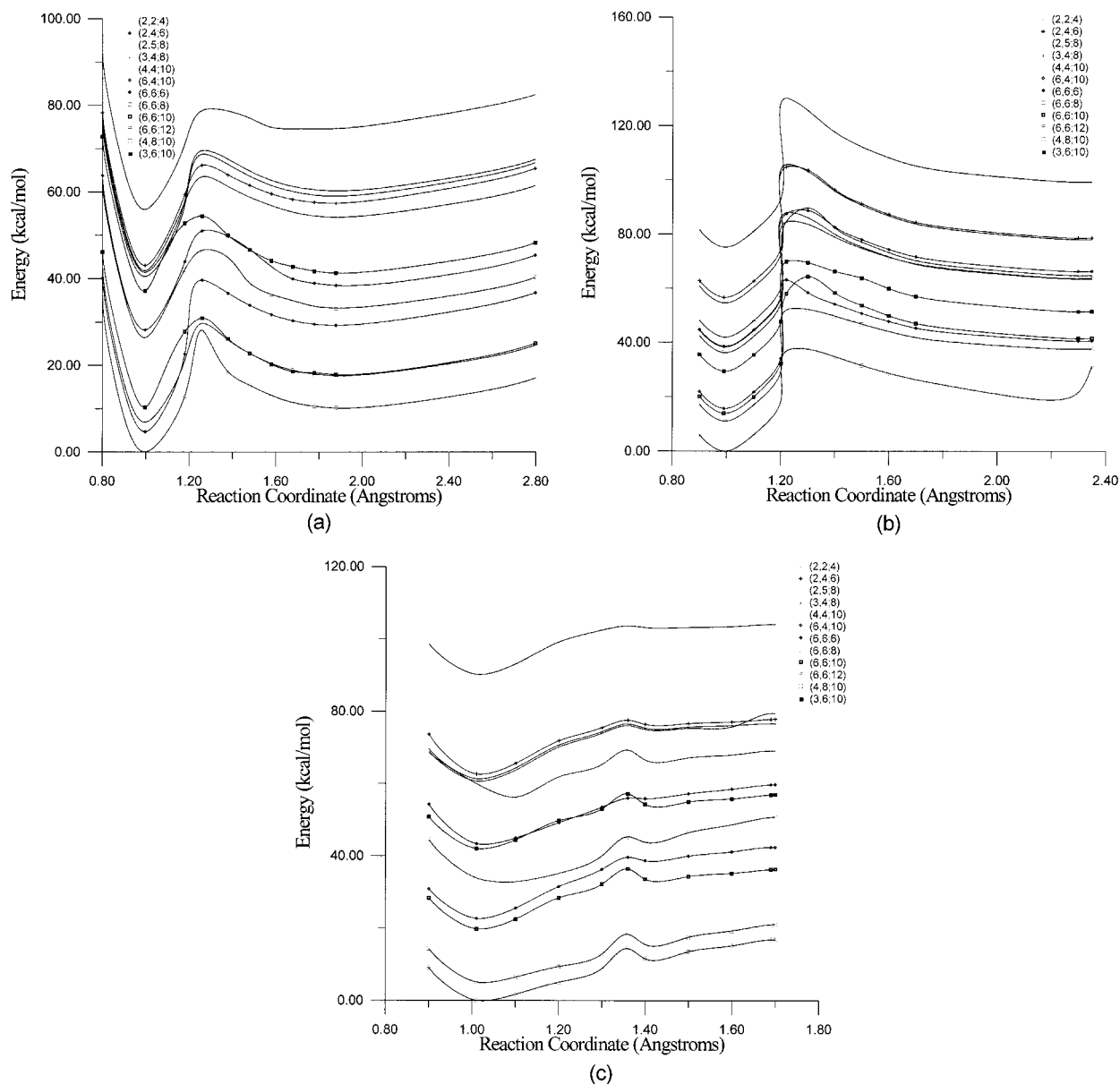


FIGURE 2. Relative energy profiles for the proton transfer reaction in 1-amino-3-propenal in: (a) the ground state, (b) the $n\pi^*$ state, and (c) the $\pi\pi^*$ state computed using the CASSCF method and the HF/CIS/D95** optimized geometries. Results for the following active spaces: (2, 2; 4), (2, 4; 6), (2, 5; 8), (3, 4; 8), (4, 4; 10), (6, 4; 10), (6, 6; 6), (6, 6; 8), (6, 6; 10), (6, 6; 12), (4, 8; 10), and (3, 6; 10) are plotted in thin plus, thick plus, thin multiply, asterisk, thin rhombus, thick rhombus, black rhombus, thin square, thick square, thin square-plus, thin square-multiply, and black square symbols, respectively.

transfer in the ground state and the two lowest-lying singlet excited states of 1-amino-3-propenal is not sensitive to the size of the active space. However, noticeable quantitative differences in the relative energy of the two tautomers and in the energy barrier for the proton transfer reaction appear among the different active spaces. The question that we would like to address is:

What is the smallest active space that still yields reliable results?

The energy barriers and the relative energies of the two tautomers obtained with the different active spaces for the ground and $n\pi^*$ states are reported in Table I. Upon inspection of the results for the ground state, we notice a large difference between the value of the energy barrier obtained

TABLE I.

Energy Difference between the Two Tautomeric Forms ΔE (keto-enol) and Energy Barrier ΔE^\ddagger (enol-TS) in kcal/mol for the Ground and $n\pi^*$ States Computed with the CASSCF Method Using Different Active Spaces and the HF/CIS/D95** Optimized Geometries.

Active Space	S_0		$n\pi^*$	
	ΔE	ΔE^\ddagger	ΔE	ΔE^\ddagger
(2, 2; 4)	18.6	4.3	24.3	30.8
(2, 4; 6)	14.5 (18.0) ^a 10.6 ^b (10.7) ^c	8.7 (9.6) ^a 13.2 ^b (13.3) ^c	22.2 (27.6) ^a 26.4 ^b (26.1) ^c	26.0 (28.7) ^a 29.0 ^b (25.3) ^c
(2, 5; 8)	12.3	9.3	23.7	27.5
(3, 4; 8)	18.8	9.3	23.0	19.9
(4, 4; 10)	18.6	9.6	24.3	20.8
(6, 4; 10)	24.6	10.4	24.9	22.6
(6, 6; 6)	10.2	12.5	27.9	21.2
(6, 6; 8)	6.8	13.3	27.4	24.3
(6, 6; 10)	7.5	13.0	27.7	16.4
(6, 6; 12)	10.1	18.0	21.7	16.1
(4, 8; 10)	10.7	12.1	26.6	14.3
(3, 6; 10)	4.2	13.1	22.2	18.4

^a The UHF / D95** optimized geometries were used in the calculations.

^b The CASSCF / D95** optimized geometries were used in the calculations.

^c The CASSCF / D95** optimized geometries were used in the calculations; results obtained with the D95++** basis set.

with the smallest active space and the energy barrier obtained with the largest active space. As the number of the active orbitals and the active electrons increase, the energy barrier slowly raises. The dependence of the CASSCF barrier heights on the choice of the active space was already pointed out by Rovira et al.²⁸ The results of the relative energy of the two tautomers behave rather erratically when the active space is enlarged. In general, the results for the smaller active spaces are fairly different from those obtained with the (6, 6; 12) active space.

In the $n\pi^*$ excited state, we see no significant differences in the relative energy of the two tautomers among the active spaces that have less than 12 orbitals. The energy difference between the two forms is approximately 3 kcal/mol larger for all the 12 orbital active spaces, except for the (6, 6; 12) space where the value is smaller. The energy barrier lowers when the number of active orbitals and electrons increase in the active space, giving the (6, 6; 12) and (4, 8; 10) active spaces the smallest values.

Following the CASSCF calculations we performed CASPT2 calculations to account for the dynamic energy effects in the proton transfer energies. Following the proton transfer reaction coordinate we found an interesting irregularity near the transition point in both excited states. Whereas one of the points near the transition state in the $n\pi^*$

excited state appears to have a bit too low energy when the CIS-optimized geometry is used, in the $\pi\pi^*$ excited state the use of the CIS geometry gives a too-high energy value for the transition point in relation to the neighboring points. As a consequence, the calculated energy values near the transition state are suspect, and we decided not to include them in the PECs. Comparing the CASPT2 PECs among the different active spaces for the ground state and the $n\pi^*$, and $^1\pi\pi^*$ excited states in Figures 3a, b, and c, respectively, we notice that they look qualitatively similar to the CASSCF curves. However, the CASPT2 energies change much less among the different active spaces than the CASSCF results.

In Table II we gathered the results of the relative energy between the oxo and the hydroxy tautomers and the energy barrier yielded by the CASPT2 calculations. The results indicate that the CASPT2 energy barrier in the ground state is reduced for every active space with respect to the corresponding CASSCF energy barrier. A similar effect of the dynamic correlation was observed before.⁴⁷ Also, the energy difference between the two tautomers in the ground state is considerably reduced in the CASPT2 method. Interestingly, CASPT2 gives more similar relative energy values for all the considered active spaces than CASSCF. It was pointed out that when the active space is large enough, the intruder state problem should

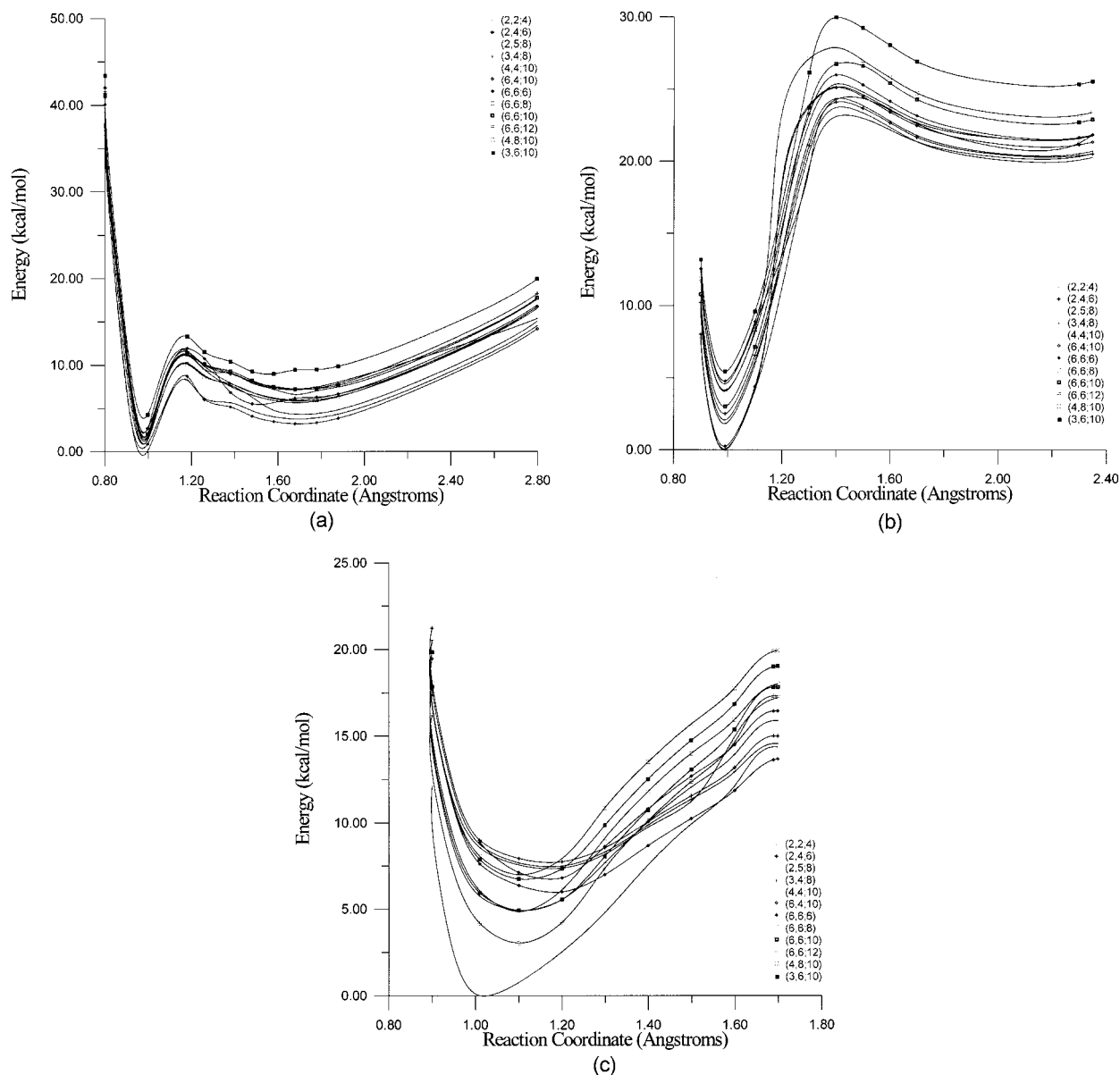


FIGURE 3. Relative energy profiles for the proton transfer reaction in 1-amino-3-propenal in: (a) the ground state, (b) the $n\pi^*$ state, and (c) the $\pi\pi^*$ state computed using the CASPT2 method and the HF/CIS/D95** optimized geometries. Results for the following active spaces: (2, 2; 4), (2, 4; 6), (2, 5; 8), (3, 4; 8), (4, 4; 10), (6, 4; 10), (6, 6; 6), (6, 6; 8), (6, 6; 10), (6, 6; 12), (4, 8; 10), and (3, 6; 10) are plotted in thin plus, thick plus, thin multiply, thin asterisk, thin rhombus, thick rhombus, black rhombus, thin square, thick square, thin square-plus, thin square-multiply, and black square symbols, respectively.

not appear and the CASPT2 results should be much less sensitive to the size of the active space.³ With any of our medium-size active spaces, (2, 4; 6), (2, 5; 8), or (3, 4; 8), we obtain quantitatively very similar CASPT2 results to those obtained with the largest active space. In general, we concur with Roos et al.^{25,26,48,49} that the CASSCF method should only include nondynamic correlation and

the dynamical correlation effects should be included via multireference CI, coupled cluster, or perturbation theory calculations.

Due to the fluctuation near the transition state in the CASPT2 $n\pi^*$ PEC it is difficult to determine the energy barrier for the proton transfer reaction in this state. However, we can definitely state that the energy barrier and the relative en-

ergy between the oxo and hydroxy tautomers are reduced when the dynamic correlation effects are added. In the $n\pi^*$ state, the basicity of the basic group is reduced because one nonbonding electron of the nitrogen or oxygen atom in the enol and keto forms, respectively, is transferred to the π^* orbital. In consequence, the hydrogen bond weakens, and this is reflected in a large barrier for the proton transfer in the $n\pi^*$ state than in the ground state.³⁹ However, the CASPT2 energy barriers obtained with the CIS-optimized geometries are, in general, lower in the $n\pi^*$ state than in the ground state, casting doubts about the description of the energy barrier by the CASPT2//CIS approach in the $n\pi^*$ state.

The energy fluctuations near the transition points in the excited states cannot be due to an incorrect selection of the active space. For all the active spaces, the weight of the reference function, w , remains large in all points of the excited-state PECs, indicating that the CASPT2 calculations are well balanced along the whole range of the reaction coordinate and free of intruder states. A possible reason for the fluctuations may be inaccuracy in the molecular geometries at the points neighboring the transition point. The CIS method, which we used to determine the geometries, probably provides not as good results for the transition point as for the equilibrium points, where the chemical bonds are not stretched. To check this supposition we calculated the CASPT2 energy curves for the ground and excited states using the (2,4;6) active space and the geometries optimized with the CASSCF and UHF methods (the $\pi\pi^*$ excited state was only calculated with the CASSCF optimized structures). The UHF method, although not spin "clean," correctly describes the separation of the electrons occurring in the bond dissociation. With the use of either the UHF or CASSCF geometries the fluctuations near the transition points in the CASPT2 energy curves disappear (see Fig. 4). This result indicates that care must be taken in choosing the method for optimizing the geometries that are used to calculate the PECs at a more sophisticated level of theory. Inaccuracy in geometries could be translated to undesired irregularities in the PECs. For example, as the present results indicate, the CIS method is not accurate enough to describe geometries near the transition state point because it produces fluctuations of the CASPT2 energies near this point.

Tables I and II allow us to analyze how the results are quantitatively affected by using geometries optimized with different methods. Both the

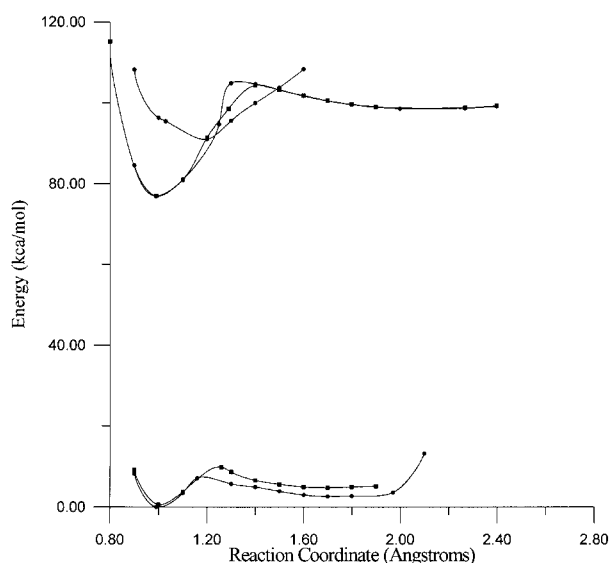


FIGURE 4. Relative energy profiles for the proton transfer reaction in 1-amino-3-propenal computed using the CASPT2 method with the (2, 4; 6) active space and with the UHF/D95** optimized geometries (square symbols) for the ground and $n\pi^*$ states and with the CASSCF/D95** optimized geometries (circle symbols) for the ground, $n\pi^*$ and $\pi\pi^*$ states.

CASSCF relative energy of the two tautomers and the energy barrier in the ground state and the $n\pi^*$ excited state increase by a few kcal/mol when the UHF geometries are used with respect to the values obtained with the HF/CIS geometries. A similar pattern occurs when the CASSCF geometries are employed, with the exception of the relative energy of the two tautomers in the ground state which decreases. The CASPT2 results are more sensitive to the used geometry in the $n\pi^*$ excited state than in the ground state. For instance, the increase of the energy barrier obtained using the UHF and CASSCF optimized geometries vs. the HF/CIS geometries is about 2 kcal/mol larger in the $n\pi^*$ excited state than in the ground state. As a result, the energy barrier is higher in the $n\pi^*$ excited state than in the ground state, as one would expect. Worth noticing is that, in general, the values obtained with the use of the UHF geometries are quite close to the values obtained with the use of the CASSCF geometries, which indicate that the UHF geometries yield reliable results. The drawback is that only the geometries of the lowest-lying state of a given symmetry or multiplicity can be optimized with the UHF method. From Tables I and II it can also be noticed that enlarging the basis sets by adding diffuse func-

TABLE II. Energy Difference between the Two Tautomeric Forms ΔE (keto-enol) and Energy Barrier ΔE^\ddagger (enol-TS) in kcal/mol for the Ground and $n\pi^*$ States Computed with the CASPT2 Method Using the Different Active Spaces and the HF/CIS/D95** Optimized Geometries.

Active Space	S_0		$n\pi^*$	
	ΔE	ΔE^\ddagger	ΔE	ΔE^\ddagger
(2, 2; 4)	5.2	3.8	17.1	2.7
(2, 4; 6)	5.1 (5.1) ^a 2.6 ^b (2.7) ^c	4.4 (4.2) ^a 4.9 ^b (4.8) ^c	17.9 (21.9) ^a 21.7 ^b (21.2) ^c	3.7 (5.5) ^a 6.3 ^b (6.5) ^c
(2, 5; 8)	3.0	5.9	18.1	3.6
(3, 4; 8)	4.2	5.3	18.7	3.9
(4, 4; 10)	4.1	5.4	20.3	2.8
(6, 4; 10)	2.4	5.5	20.9	3.9
(6, 6; 6)	2.9	6.4	17.0	4.3
(6, 6; 8)	4.0	5.1	17.5	3.8
(6, 6; 10)	5.2	4.1	19.7	4.0
(6, 6; 12)	3.8	4.5	21.2	3.9
(4, 8; 10)	4.5	4.3	19.1	4.6
(3, 6; 10)	4.2	4.8	20.0	4.6

^a The UHF / D95** optimized geometries were used in the calculations.

^b The CASSCF / D95** optimized geometries were used in the calculations.

^c The CASSCF / D95** optimized geometries were used in the calculations; results obtained with the D95++** basis set.

tions has a minor effect on the CASSCF/CASPT2 energies.

Conclusions

The effect of the choice of the active orbital space in the CASSCF and CASPT2 calculations on the PECs describing the proton transfer reaction in 1-amino-3-propenal in the ground state and the two lowest-lying single excited states has been analyzed. The results lead to the following conclusions:

1. The qualitative description of the proton transfer in 1-amino-3-propenal in the ground state and the excited states obtained with the CASSCF and CASPT2 calculations does not strongly depend on the number of active orbitals and on the number of active electrons.
2. From a quantitative point of view, the medium-size active spaces (2, 4; 6), (2, 5; 8), and (3, 4; 8), should be sufficient to describe the ESIPT in systems similar to 1-amino-3-propenal. The CASSCF calculation should only include the nondynamic electron correlation, and the dynamical correlation effects should

be included via multireference CI, coupled-cluster, or perturbation theory calculations.

3. Care must be taken in choosing the method to optimize the molecular geometry along the reaction coordinate. When the CIS-optimized geometries are used, the CASPT2 energy curves for the excited states show fluctuations near the transition point. The UHF or the CASSCF methods are better alternatives for geometry optimizations.

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